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Solar photocatalytic abatement of sulfamethoxazole over Ag_3PO_4/WO_3 composites

Eleni Grilla[a], Athanasia Petala[a], Zacharias Frontistis[a], Ioannis K. Konstantinou[b], Dimitris I. Kondarides[a], Dionissios Mantzavinos[a,*]

[a] *Department of Chemical Engineering, University of Patras, Caratheodory 1, GR-26504 Patras, Greece*
[b] *Department of Chemistry, University of Ioannina, GR-45110 Ioannina, Greece*

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ABSTRACT

Ag_3PO_4/WO_3 composites with Ag_3PO_4:WO_3 molar ratios of 85:15, 75:25, 60:40, 40:60 and 25:75 were synthesized, characterized and tested for the degradation of the antibiotic agent sulfamethoxazole (SMX) under simulated solar radiation. The composites were characterized employing the BET, XRD, UV–vis DRS, SEM-EDS and TEM techniques. Changes in SMX concentration with irradiation time were followed by HPLC.

Of the various materials tested, the Ag_3PO_4/WO_3(75:25) sample (1 m^2/g specific surface area, 2.41 eV band gap energy) exhibited the highest activity with 90% SMX conversion (525 μg/L initial concentration and 200 mg/L photocatalyst) achieved in just 2 min. Process efficiency was found to increase with increasing photocatalyst concentration (25–200 mg/L) and decreasing SMX concentration (2100–260 μg/L). SMX degradation in ultrapure water (UPW) was faster than in bottled water and treated domestic wastewater containing various inorganic and organic constituents; however, certain matrix constituents such as chloride, bicarbonate and humic acid had no or even a positive effect on degradation.

The addition of hydroxyl radical scavengers (t-butanol, DMPO) in excess did not affect SMX degradation, while the opposite phenomenon occurred using a hole scavenger (EDTA), which suppressed degradation. In parallel, no hydroxylated or oxygenated transformation products (TPs) were detected by UPLC-ESI-MS analysis.

The Ag_3PO_4/WO_3(75:25) sample suffered photo-corrosion resulting in the formation of metallic silver, as well as partial metal leaching in the aqueous phase, both of which contributed to a gradual loss of activity upon repeated use.

1. Introduction

Semiconductor photocatalysis has been widely tested to eliminate trace contaminants in water matrices. Since the discovery of TiO_2 as an effective photo-electrode for water splitting in 1970s, most researchers have focused on TiO_2 and TiO_2-based catalysts for environmental applications, since titania is a photoactive, inexpensive, readily available, stable and non-toxic material. Nonetheless, TiO_2 photocatalysis suffers a serious drawback associated with its wide bandgap energy (3.0–3.2 eV) which overlaps only with the UV region of the electromagnetic spectrum [1].

In quest of new materials that could be highly responsive in the visible, thus exploiting renewable solar energy to induce photocatalytic reactions, Yi et al. [2] reported for the first time the unique photocatalytic properties of silver orthophosphate (Ag_3PO_4) for water splitting and the degradation of methylene blue under visible light. This photocatalyst was substantially more active than other visible light-responsive catalysts, such as $BiVO_4$, WO_3 and $TiO_{2\text{-}x}N_x$, since it could achieve a quantum efficiency of up to 90% at wavelengths in the range 400–480 nm, thus implying a very low electron-hole recombination rate [1–3]. Since the pioneering work of Yi et al. [2], some research efforts have focused on the synthesis and characterization of Ag_3PO_4-based materials, whose photocatalytic activity in the visible spectral region has been evaluated using mostly organic dyes as the probe material [4–8].

Our group has recently reported for the first time the use of Ag_3PO_4 [9] and Ag_3PO_4/TiO_2 composites [10] for the degradation of trace contaminants of emerging concern, namely xenoestrogens. The rationale behind the use of Ag_3PO_4/TiO_2 composite materials has to do with increased levels of catalyst activity and stability associated with more efficient charge separation, as well as greater specific surface areas of the composites compared to Ag_3PO_4. Complete degradation of 220 μg/L

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[*] Corresponding author.
E-mail address: mantzavinos@chemeng.upatras.gr (D. Mantzavinos).

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bisphenol A using a composite with a Ag_3PO_4:TiO_2 molar ratio of 75:25 could be achieved in just 4 min of simulated solar irradiation, i.e. over three times faster than with Evonik P-25 TiO_2 and twice faster than with pure Ag_3PO_4 [10].

A major issue associated with Ag_3PO_4 is its photochemical instability since, in the absence of appropriate electron scavengers in the solution, the photocatalyst is irreversibly reduced to metallic silver [2,11]. This was observed in our previous work [10], where silver ion reduction occurred for both pure Ag_3PO_4 and Ag_3PO_4/TiO_2 catalysts; however, the latter retained greater catalytic activity than the former. Zhang et al. [12] synthesized Ag_3PO_4/WO_3 composites and tested them for the decomposition of organic dyes under visible light radiation. They found that the composites were substantially more active than their individual components for the above reaction and, more importantly, they suffered minimum silver ion reduction to metallic silver (although reduction was not completely impeded). Since the conduction band (CB) minimum of tungsten trioxide (0.64 V vs. NHE) is more positive in the electrochemical scale than that of Ag_3PO_4 (0.45 V vs. NHE), the photogenerated electrons are expected to move from the CB of Ag_3PO_4 to that of WO_3, which would avoid the formation of metallic silver on the surface of the photocatalyst [11]. Similarly, Chang et al. [13] reported only 5% metallic silver formation on the surface of a Ag_3PO_4/WO_3 composite used for rhodamine photocatalytic degradation, while the respective value was over 27% for pure Ag_3PO_4.

In this perspective, our group synthesized, characterized and tested Ag_3PO_4/WO_3 composite materials of variable Ag_3PO_4:WO_3 content for the photocatalytic degradation of sulfamethoxazole (SMX), a pharmaceutical agent belonging to the group of sulfonamide antibiotics. SMX was chosen as a model trace contaminant since it is probably the most commonly employed antibiotic of this group and it is widely prescribed to treat human and animal infections. The fate of antibiotics, amongst other pharmaceuticals, in the aquatic environment (their occurrence has been reported in surface water, seawater, groundwater, as well as in soils and sediments [14,15]) has attracted enormous attention in recent years because antibiotics are biologically active and, therefore, they cannot be efficiently removed in conventional wastewater treatment plants. Moreover, the increase in antibiotics consumption and their subsequent release into the environment over the past few decades has resulted in the generation of bacteria that are strongly resistant to antibiotics [16,17].

Although there have been a few studies regarding the use of Ag_3PO_4/WO_3 composite materials for the photocatalytic degradation of organic dyes and phenol [12,13,18–20], this is, to the best of our knowledge, the first report on the degradation of a pharmaceutical micro-contaminant of environmental concern by photocatalysis over Ag_3PO_4/WO_3 composites or, indeed, any other Ag_3PO_4-based material.

In this work, the influence of catalyst composition and of process parameters, such as catalystconcentration, antibiotic concentration, type of radiation and quality of actual and synthetic water matrices on SMX degradation kinetics was investigated. Issues associated with degradation pathways and catalyst stability are also discussed.

2. Materials and methods

2.1. Chemicals and water matrices

Sulfamethoxazole (SMX: $C_{10}H_{11}N_3O_3S$) was purchased from Sigma–Aldrich (CAS no: 72 3-4 6-6) and used as received. Sodium tungstate dihydrate ($Na_2WO_4{\cdot}H_2O$, CAS no: 10213-10-2) and ammonium chloride (NH_4Cl, CAS no: 12125-02-9) were supplied by Sigma–Aldrich, silver nitrate ($AgNO_3$, CAS no: 7761-88-8) was supplied by Alfa Aesar and sodium dihydrogen phosphate monohydrate ($NaH_2PO_4{\cdot}H_2O$, CAS no: 10049-21-5) was supplied by Merck Millipore. Ethylenediaminetetraacetic acid (EDTA, CAS no: 60-00-4) and t-butanol (CAS no: 75-65-0) were purchased from Sigma–Aldrich, while 5,5dimethyl-1-pyrroline-*N*-oxide (DMPO, CAS no: 3317-61-1) was purchased from Cayman Chemical.

Most of the experiments reported here were carried out in ultrapure water (UPW, pH = 6) taken from a water purification system (EASYpure RF-Barnstead/Thermolyne, USA). Other matrices included (i) commercially available bottled water (BW: pH = 7.6, 475 μS/cm conductivity containing 286 mg/L bicarbonate, 8.2 mg/L chloride, 9.6 mg/L sulfate, 7.9 mg/L nitrate and 102.7 mg/L various metal ions), (ii) secondary treated wastewater (WW) taken from the university campus treatment plant (pH = 8, total organic carbon = 8.8 mg/L), and (iii) UPW spiked with various water constituents such as humic acid (CAS number 1415-93-6), bicarbonate (CAS no: 144-55-8) and chloride (CAS no: 7647-14-5); all of them were purchased from Sigma–Aldrich.

2.2. Preparation of photocatalysts

The Ag_3PO_4/WO_3 composites were prepared by a deposition-precipitation process. An appropriate amount of $Na_2WO_4{\cdot}H_2O$ was dissolved in 25 mL of triply distilled water (solution A), whereas 1.91 g of NaH_2PO_4 was dissolved in 25 mL of UPW (solution B). After stirring for 15 min, solutions A and B were added in an aqueous solution (50 mL) of $AgNO_3$ (3.06 g). The resulting mixture was left under vigorous stirring for 4 h at room temperature. The obtained precipitate was collected by filtration, washed with triply distilled water for several times and then dried in an oven at 60 °C for 12 h. Composites with different molar ratios of Ag_3PO_4 to WO_3 were prepared varying the amount of $Na_2WO_4{\cdot}H_2O$ in the starting solution, while keeping constant the content of Ag_3PO_4. The photocatalysts thus prepared are denoted in the following as Ag_3PO_4/WO_3 (*x*:*y*), where *x*:*y* is the molar ratio of Ag_3PO_4 to WO_3.

Pure Ag_3PO_4 was prepared using the same method but in the absence of $Na_2WO_4{\cdot}H_2O$.

Pure WO_3 was prepared according to a hydrothermal method reported by Zhang et al [12]. Briefly, appropriate amounts of $Na_2WO_4{\cdot}H_2O$ (0.05 M) and NH_4Cl (0.5 M) aqueous solutions were mixed and placed in a 90 mL teflon-lined stainless steel autoclave and kept at 180 °C for 48 h. The precipitate was obtained by centrifugation, washed with distilled water and dried at 70 °C for 12 h. Finally, WO_3 was obtained after calcination at 500 °C for 2 h.

2.3. Catalyst characterization

The as prepared photocatalysts were characterized by (i) X-Ray diffraction (XRD) using a Philips P (PW 1830/40) instrument employing Cu Ka source (λ = 1.5406 Å), (ii) nitrogen physisorption at liquid nitrogen temperature (B.E.T. method) on a Micromeritics Gemini III 2375 analyzer, (iii) UV–vis diffuse reflectance spectroscopy (DRS) in the range of 200–800 nm with a UV–vis spectrophotometer (Varian Cary 3), (iv) scanning electron microscopy (SEM) using a JEOL 6300 microscope equipped with an energy dispersive spectrometer (EDS), and (v) transmission electron microscopy (TEM) with a JEOL JEM-2100 system, operated at 200 kV. The characterization techniques and procedures have been described in detail elsewhere [10].

2.4. Experimental procedure

In a typical run, 120 mL of an aqueous solution containing, unless otherwise stated, 525 μg/L SMX were loaded in the cylindrical reaction vessel under continuous stirring at 400 rpm. This SMX concentration was chosen to (i) match realistically those typically found in environmental samples (i.e. between ng/L and low μg/L levels), and (ii) facilitate SMX quantitation with the analytical protocols/techniques available in this work. The appropriate amount of catalyst was then added and the solution was left to equilibrate in the dark for 15 min. The solar simulator (Oriel, model LCS 100 equipped with a 100 W xenon, ozone-free lamp) was then turned on and samples of 1.2 mL were periodically